

Study the Atomic Properties for N^{+5} and O^{+6} Ions

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Abstract

The aim of this paper is to study the effect of electron correlation for the uncorrelated Hartree-Fock (HF) and correlated Configuration-Interaction (CI) wave functions for N^{+5} and O^{+6} ions. To this end, the address discuss the physical properties of the one-particle radial distribution function $D(r_1)$ as well as the expectation value of the one-particle distribution function $\langle r_1^n \rangle$. We conclude that the one-particle radial distribution function and the expectation values for $n=1, 2$ increase as increase the atomic number Z . Indeed, the effect of electron correlation increase with increase the atomic number Z .

Key World: Hartree-Fock, Configuration interaction, and Electron correlation

دراسة الخواص الذرية لأيوني N^{+5} و O^{+6}

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الخلاصة

الهدف من هذا البحث هو دراسة تأثير الترابط الالكتروني لدالة هارترى-فوك غير المترابطة مع دالة كثافة التوزيع المترابطة لأيوني N^{+5} و O^{+6} . تم التطرق ايضا الى مناقشة دالة توزيع الكثافة القطرية $D(r_1)$ و القيم المتوقعة $\langle r_1^n \rangle$ لتلك الكثافة لجسيم واحد. من خلال نتائج البحث استنتجت ان دالة توزيع الكثافة و القيم المتوقعة عندما $n=1,2$ لجسيم واحد تزداد بزيادة العدد الذري Z . بالاضافة الى ذلك تأثير الترابط الالكتروني يزداد بزيادة العدد الذري Z .

I. Introduction

The Hartree-Fock (HF) approximation is a much useful method to study the electronic structure of atoms and molecules [1, 2]. The N-electron wave function of the HF approximation can be

written as the antisymmetrised product of N one-electron functions or orbitals [2], where the one-electron function is a computationally and conceptually attractive simplification in the description of the N-electron system. In the HF orbitals calculation the instantaneous interaction between the electrons is replaced (approximated) by the interaction of an electron with the average field generated by the other N-1 electrons. Indeed, the correlation of the electronic repulsion (Coulomb correlation) is neglected in the HF approximation [3, 4]. This is the Hartree Fock error or correlation error. Coulomb correlation can be included in the calculation, for instance, through configuration interaction (CI) but, compared to the HF, this is computationally much more complex and time-consuming [5, 6].

Several research have instigated a broad interest in the Hartree-Fock and configuration interaction wave functions, and paved the way for extensive studies of a wide range of both experimental and theoretical topics. In Ref. [7] was generalized the self-consistent field (SCF) formalism. Ref. [8] was obtained an accurate wave function for the ground state of atomic systems. The successful approaches of many-particle quantum mechanics for the ground and excited states of Helium, Lithium and Beryllium atoms using a configuration interaction approximation was done by Ref. [9]. In particular, Ref. [10] was analyzed and compared five wave functions for Hydrogen ion, and discussed the two-particle density.

To this end, this paper deals with the effect of electron correlation due to the coulomb repulsion between electrons. Therefore, we start with the uncorrelated HF and correlated CI wave functions, respectively, in Sec. II. In Sec. III. I discuss the atomic properties of the two-particle density for HF and CI wave functions, respectively, as well as one-particle radial distribution function $D(r_1)$, and the expectation value for the one-particle radial distribution function $\langle r_1^n \rangle$. Finally, I mention and summarize the result in Sec. IV.

II. Wave Functions

A. Hartree-Fock Wave Function

The total wave function of the independent practical model is given by Slater determinant:

$$\Psi_{HF}(x_1, x_2, \dots, x_N) = |\Phi_1(x_1) \Phi_2(x_2) \dots \Phi_N(x_N)|, \dots \dots (1)$$

With the single electron wave function $\Phi_i(x_i)$ and x_i denotes spin-orbital components

$$\Phi_i(x_i) = \phi_i(r_i)\alpha(\delta)\dots\dots (2)$$

r_i denotes the radial and angular co-ordinate, while $\alpha(\delta)$ is the spin wave function. The spatial part $\phi_i(r_i)$ can be written as an expansion in some set of analytic basis functions [11]:

$$\phi_{nl}(r) = \sum_i c_n^i \chi_{nl}^i \dots\dots (3)$$

Where c_n^i is a coefficient taken to minimize the energy. The basis set of one-electron function (basis function) consist to be normalized Slater-type orbital defined by:

$$\chi_{nlm}(r, \theta, \vartheta) = R_{nl} Y_m^l(\theta, \vartheta) \dots\dots (4)$$

Where R_{nl} and $Y_m^l(\theta, \vartheta)$ represent the radial and angular parts, respectively. The radial part is given by:

$$R_{nl}(r) = \frac{(2\zeta)^{n+\frac{1}{2}}}{\sqrt{2n!}} r^{n-1} e^{-\zeta r} \dots\dots (5)$$

$n, l, \text{ and } m$ are quantum numbers, with exponential parameter ζ . For the HF ground state calculations of N^{+5} and O^{+6} ions I used data (C, ζ , and n) introduced in Ref. [12]. Furthermore, the ground state data for the correlated wave function of N^{+5} and O^{+6} ions have taken in Ref. [13].

B. Configuration-Interaction Wave Function

Configuration interaction (CI) is one of the most general ways to improve upon Hartree–Fock theory by adding a description electron correlation in term of correlation energy. Simply put, a CI wave function is a linear combination of Slater determinants (or spin-adapted configuration state functions), with the linear coefficients being determined variationally via diagonalization of the Hamiltonian in the given subspace of determinants [14]. The correlation description of the ground state of N^{+5} and O^{+6} ions have taken from Weiss [13, 15]. Partitioning technique is used to describe the correlation effects.

$$\Psi_{CI} = \sum_i c_i \phi_i \dots\dots (6)$$

Where each of ϕ_i s (configurations) is antisymmetrized product of one-electron functions (spin orbital), and the coefficients c_i are taken from minimizing the total energy. Applying the variation theorem and solving an infinite set of secular equations may in principle, obtain the exact wave function. In this work we have used the Weiss method of configuration interaction (CI) [6]. The specific form of the configuration system studied to be linear combination of single Slater determinant using fifteen configuration of s symmetry.

$$(\lambda\kappa) = \frac{1}{\sqrt{2}} \sum |\lambda(1)\alpha\kappa(2)\beta| \dots \dots (7)$$

The basis set of one-electron function consist to be normalized Slater-type orbital defined in Refs. [7-9].

III. Atomic properties for N^{+5} and O^{+6} Ions

A- One-particle distribution Function and Electron correlation $\Delta D(r_1)$

The one-particle radial distribution function for the correlated CI and uncorrelated HF wave functions has the form [15]

$$D_{HF}(r_1) = \int_0^\infty \gamma_{HF}(r_1, r_2) r_1^2 r_2^2 dr_2 \dots \dots (8)$$

$$D_{CI}(r_1) = \int_0^\infty \gamma_{CI}(r_1, r_2) r_1^2 r_2^2 dr_2 \dots \dots (9)$$

where $\gamma_{CHF}(r_1, r_2)$ and $\gamma_{CI}(r_1, r_2)$ are the two particle density for uncorrelated and correlated wave. To calculate the electron correlation for the one-particle distribution function, we have to take the difference between the correlated and uncorrelated wave function which has the form

$$\Delta D(r_1) = D_{CI}(r_1) - D_{HF}(r_1) \dots \dots (8)$$

B- The one-particle expectation value $\langle r_1^n \rangle$

The one-particle expectation value has the form $\langle r_1^n \rangle$ [11, 16]

$$\langle r_1^n \rangle = \int_0^\infty D_i(r_1) r_1^n dr_1 \dots \dots (11)$$

IV. Results and Discussions

The results of this paper achieve by using of Mathematica Program version (2010). Furthermore, A. Sarsa, F.J. Gálvez, and E. Buendía have used for Hartree-Fock [12] wave function and Weiss for Configuration-Interaction wave function [13].

A. The One-Particle Radial Distribution Function.

The one-particle density distribution function $D(r_1)$ represents the probability of finding the test electron at distance r_1 from the nucleus (where the nucleus is fixed at origin point of axis).

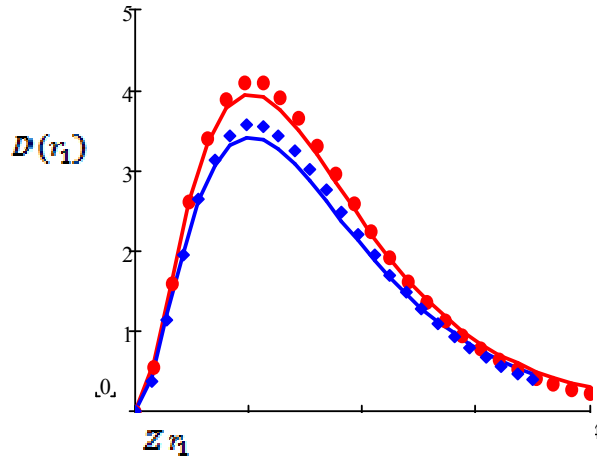


Figure 1: The One-particle radial distribution function $D(r_1)$ in unit of (a. u.) for N^{+5} (blue curves) and O^{+6} (red curves) ions using uncorrelated HF (solid lines) and correlated CI (dotted lines) wave functions.

To this end, Figure 1 shows the one-particle radial distribution function $D(r_1)$ versus r_1 . Solid curves correspond to the uncorrelated (HF) wave function and dotted curves represent to the correlated (CI) wave function of N^{+5} (blue curves) and O^{+6} (red curves). Indeed, Fig. 1 shows that the probability increases with the increase the distance r_1 , then decrease after ($r_1 = .015$) and ($r_1 = .013$) for N^{+5} and O^{+6} , respectively, until reaches zero which means that the probability to fining the electron occurs at a distance ($r_1 = .015$) and ($r_1 = .013$) for N^{+5} and O^{+6} , respectively. This happens due to the anti-parallel spin component, therefore, two electrons will be close to each other. We see a difference between solid and dotted curves due to the correlation effect which considered in the configuration interaction wave function.

The interesting phenomena is the correlation effect on $D(r_1)$ in Fig. 2 which represents the difference $\Delta D(r_1)$, between the correlated wave function (CI) and the uncorrelated wave function (HF) as a function of r_1 . The difference shows an increase in $D(r_1)$ and then a decrease in $D(r_1)$, this change caused by the correlation effect. The correlation effects come from the separation of two electrons of this shell, where we put each one in virtual state (configuration) for instance ((1s2s), (2s2s)...). Figure 2 shows that the correlation increase as increase the atomic number Z .

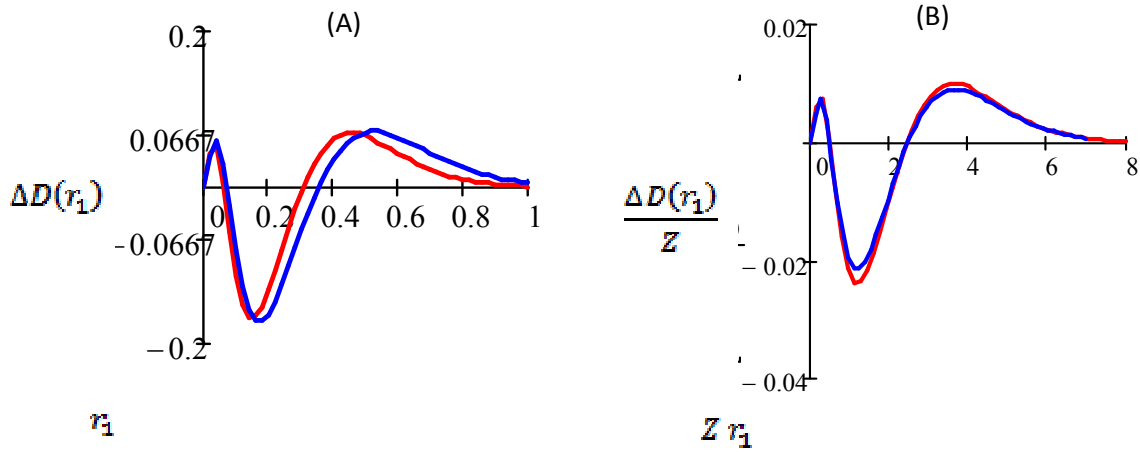


Figure 2: Electron correlation of one-particle radial distribution function $\Delta D(r_1)$ in unit of (a. u.) as a function of r_1 (A) and $Z r_1$ (B), respectively, for N^{+5} (blue curves) and O^{+6} (red curves) ions using uncorrelated HF and correlated CI wave functions.

B. The One-Particle Expectation Value

Table I shows the one-particle expectation value $\langle r_1^n \rangle$ as a function of the exponent parameter $n = -2.2$. In addition Fig. 3 shows the one-particle expectation value $\langle r_1^n \rangle$ as a function of exponent parameter $n = -2.2$ of the uncorrelated HF (solid curves) and correlated CI (dotted points) wave functions for N^{+5} (blue curves) and O^{+6} (red curves) ions. We can see in Fig. 3 that the expectation value of one-particle decrease with increase n . In this paper the value of n is important parameter because we can understand some physical properties of N^{+5} (blue curves) and O^{+6} (red curves) ions that mention in table 1 and Fig. 3. To this end, $n = -2$ shows

the force between the electron and nucleus, $n = -1$ gives the electron-nuclear attraction energy. In particular, $n = 0$ refers to the normalization constant of the wave functions and finally $n = 2$ is important to measure the diamagnetic susceptibility. We note the uncorrelated HF wave function for $n = -2, -1, 0$ is smaller the correlated CI wave function as well as for $n = 1, 2$ shows that uncorrelated HF wave function is larger the correlated CI wave function due to electron correlation where the correlated CI wave function takes into account the regulation forces between the electrons.

Table I: the one-particle expectation value in unit of (a. u.) for N^{+5} and O^{+6} using uncorrelated HF and correlated CI wave functions.

Atom or Ions	Wave functions	$\langle r_1^n \rangle$ a. u.				
		n=-2	n=-1	n=0	n=1	n=2
N^{+5}	HF	90.572	6.687	1.0001	0.226	0.068
	CI	94.386	6.653	1.0001	0.237	0.078
O^{+6}	HF	119.488	7.654	1.0001	0.196	0.051
	CI	123.647	7.687	1.0001	0.205	0.058
	Ref [6]	119.487	7.687	1.0001	0.196	0.051

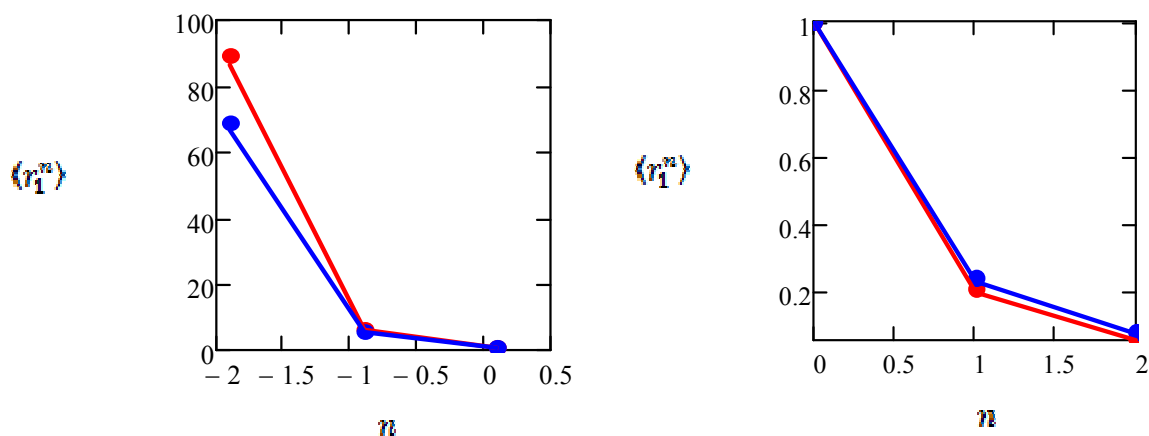


Figure 3: The one-particle expectation value $\langle r_1^n \rangle$ in unit of (a. u.) versus the power n for N^{+5} (blue curves) and O^{+6} (red curves) ions. Solid curves represent the uncorrelated HF wave function and dotted points show the correlated CI wave function, respectively.

C. Conclusions

We have studied in detail how the effect of the electron correlation changes the one-particle radial as well as the expectation value of the radial distribution function. The effect of electron correlation increase with increase the atomic number Z .

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